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DETERMINING AND ANALYZING THE STRENGTH AND IMPACT RESISTANCE OF HIGH MODULUS GLASS

by

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Determining and Analyzing the Strength and Impact of High-Modulus Glass

SUMMARY

The latest experimental glass composition to be prepared as a monofilament and then used to form a number of glass fiber-epoxy resin composite test samples is UARL 417. Tests of these UARL 417-epoxy resin composites in comparison to similar composites made with the DuPont experimental organic fiber PRD-49-I show that the UARL 417 composites have a compressive strength 4 1/2 times higher as well as specific compressive strength at least 2 1/2 times greater. Notched Charpy impact specimens prepared from the UARL 417-epoxy resin composites have impact strengths 50% greater than impact specimens from the DuPont fiber PRD-49 epoxy resin composites. Further, as shown in our last quarterly report, K911105-1, the UARL 417 glass fiber-epoxy resin composites are superior to similar composites made with the DuPont fiber PRD-49-I in flexural strength, bending stress-strain behavior, short-beam shear strength, tensile strength, and tensile stress-strain behavior.

Research continues on the question of why a given glass should have an impact strength superior to other glasses. Tests carried out using unnotched Charpy impact samples of bulk glass give an extremely preliminary indication that glasses containing both an appreciable amount of zinc oxide and aluminum oxide tend to have higher impact resistances than other glasses. Glasses to which only aluminum oxide is added do not have any increased impact resistance nor do glasses which contain only zinc oxide but no alumina.

A number of new glass compositions have been prepared in this quarter with increased emphasis on preparations without beryllia. In contrast to our recent research which emphasized cordierite-rare earth systems and invert-analog systems of glass compositions, this work like our very early research covers a number of glass fields including the eutectics and mullite-rare earth areas.

INTRODUCTION

This report is the second quarterly report for the new UARL-NASA Headquarters contract NASW-2209, Determining and Analyzing the Strength and Impact of High-Modulus Glass. This contract is the successor to the prior UARL-NASA contracts NASW-1301, Investigation of the Kinetics of Crystallization of Molten Binary and Ternary Oxide Systems, and NASW-2013, Investigation of the Kinetics of Crystallization of Several High Temperature Glass Systems. The time period covered by the present report is May 1 through July 31, 1971.

Under the earlier NASA contracts UARL studied the rate of crystallization of several unusual molten oxide systems not normally used for glass production. The two most interesting of these systems were the cordierite-rare earth oxide and the invert analog-rare earth oxide fields with both of these systems at times including beryl additions. In each of these systems a number of high-modulus high-strength glass compositions were found and some of these compositions could be fiberized by the usual rare-metal bushing drawing technique. The fibers thus produced were used to form glass fiber-epoxy resin composites and these were characterized as fully as possible. The strength and impact characteristics of the high-modulus glasses in bulk form were not investigated however.

The present contract has as its purpose a more systematic investigation of the properties of bulk samples of those high-modulus glasses previously developed and an attempt to correlate such properties with composition and microstructure. Further new compositions will also be prepared and studied both in bulk and as fibers if they show promising viscosity-temperature relationships. These investigations hopefully will contribute in a small part to the need for more information about glass in massive form that the National Advisory Board of the National Research Council has indicated (Refs. 1,2) to be a prerequisite for the successful use of glass as an engineering material.

NEW GLASS COMPOSITIONS

The thirty-nine glass compositions prepared in this period are shown in Table I. It will be noted that only seven of these thirty-nine formulas contain beryllia in agreement with our current emphasis on the preparation of a non-toxic ingredient glass whose properties are at least as good as those of UARL 344 and 417. As mentioned in our last quarterly report, glasses 473, 474, and 475 are base glasses from which glass-ceramics of high modulus were prepared by McMillan (Ref. 3) and were melted to find out if the action of pulling fibers furnished a sufficient heat treatment to develop crystals in such phosphate catalyzed glass-ceramics. Unfortunately at maximum furnace temperature, 1700°C, which was felt to be safe for the aged Super-Kanthal* elements in our platform furnace, these glasses were much too stiff to allow either fiber formation or aspiration of rods for modulus evaluation. At this temperature these glasses had the consistency of a very heavy grease. We were unable, therefore, using these compositions to answer our question concerning the contribution made by a relatively few crystals to the resultant modulus and strength of a glass fiber.

Composition UARL 476 is derived from Bastian, U.S. Patent 2,978,341 by taking maximum amounts of the important ingredients mentioned and is intended to supply a comparison of one of the most readily fiberizable high beryllia content glasses previously developed with the current UARL experimental glasses. While this glass does not yield as high a value for Young's modulus as do our glasses, its specific modulus is believed to be outstanding because of the very low value of density claimed.

*Registered trademark, The Kanthal Corporation, Bethel, Connecticut

Table I

New Glass Compositions Expressed in Mol %

Actual Ingredient	460	461	462	463	464	465
SiO_2	25	25	25	25	25	25
MgO	13	13	12	12	15	14
Li_2O	13	13	12	13	15	14
CaO	13	13	13	13	15	14
ZnO	13	13	12	13	10	8
B_2O_3	13	13	12	12	15	15
Y_2O_3	10	--	10	10	5	10
TiO_2	--	--	4	2	--	--
ZrO_2	--	10	--	--	--	--

	466	467	468	469	470	471
SiO_2	25	25	25	25	25	40.5
Al_2O_3	--	8	8	8	8	14.5
MgO	15	15	15	15	15	29.0
Li_2O	15	10	7	5	15	8.0
CaO	15	15	15	15	10	--
ZnO	15	15	15	15	15	--
B_2O_3	12.5	5	8	10	5	--
Y_2O_3	2.5	7	7	7	7	8.0

	472	473	474	475	476	477
SiO_2	40.5	78.78	78.0	70.1	36.5	57
Al_2O_3	6.5	--	3.9	--	--	12
MgO	29.0	--	--	--	12.7	4
Li_2O	8.0	12.0	12.1	10	12.0	--
CaO	8.0	--	--	--	12.8	--
ZnO	--	7.5	--	20	--	--
Y_2O_3	8.0	--	--	--	--	10
P_2O_5	--	1.00	3.00	--	--	--
K_2O	--	0.72	3.00	--	--	--
ZrO_2	--	--	--	--	0.8	--
TiO	--	--	--	--	5.1	--
$CoO(Co_2O_3)$	--	--	--	--	1.7	1.0
BeO	--	--	--	--	18.4	16

Table I (Cont'd)

Actual Ingredient	478	479	480	481	482	483
SiO_2	60	65	55	55	65	65
Al_2O_3	10	4	--	17	12	17
MgO	4	4	4	17	12	7
CaO	--	--	12	--	--	--
Y_2O_3	10	8	10	10	10	10
$CoO(Co_2O_3)$	3	1	1	1	1	1
BeO	13	16	16	--	--	--

	484	485	486	487	488	489
SiO_2	65	62	58	59	49	47
Al_2O_3	7	12	12	10	10	22
MgO	17	12	10	10	10	17
Li_2O	--	3	--	--	--	3
CaO	--	--	10	10	10	--
ZrO_2	--	--	--	--	--	2
Y_2O_3	10	10	10	10	10	3
$CoO(Co_2O_3)$	1	1	--	1	1	--
BeO	--	--	--	--	10	--
Cu_2O	--	--	--	--	--	6

	490	491	492	493	494	495
SiO_2	51	47	47	45	65	57
Al_2O_3	17	17	17	17	--	--
MgO	17	17	17	17	12	12
Li_2O	3	3	3	3	--	--
CaO	--	--	--	--	12	12
ZnO	--	--	6	6	--	8
Y_2O_3	6	10	10	10	10	10
$CoO(Co_2O_3)$	--	--	--	--	1	1
Cu_2O	6	6	--	2	--	--

Table I (Cont'd)

Actual Ingredient	496	497	498
SiO_2	36	40	56
Al_2O_3	--	--	74
MgO	12	14	--
Li_2O	9	12	2
CaO	12	18	22 1/4
Y_2O_3	10	10	10
TiO_2	4	4	--
Co(Co_2O_3)	2	2	2
BeO	15	--	--

Other glasses of Table I as may be seen represent wide departures from the cordierite-rare earth, invert analog-rare earth, and Morey's rare-earth glass fields that formed the subject of much of UARL's earlier research. While these glasses are far from evaluated as yet especially with respect to modulus and strength, they appear to be outstanding in the ease with which they form uniform homogeneous glasses that are readily fiberizable and which have good working characteristics.

RECENT DETERMINATIONS OF YOUNG'S MODULUS OF BULK GLASS SAMPLES

Using techniques earlier described in our report, K910939-4 (Ref. 4) aspirated circular rod bulk glass samples were prepared from some of the newer UARL experimental glasses and their moduli measured by ultrasonic technique. The results of these studies are shown in Table II. It can be seen that none of the glasses recently measured have absolute values of moduli as high as the earlier UARL glasses where a number of glasses had moduli of 20 million psi or higher. On the other hand some had specific moduli which compared favorably with those found in prior UARL research.

EFFECT OF COMPOSITION ON COMPARATIVE IMPACT RESISTANCE OF BULK GLASS SAMPLES

Table III lists both the impact resistance of a number of glasses together with their composition. The impact values listed were measured on hybrid sized unnotched Charpy samples prepared directly from aspirated circular rods of bulk glass, 0.310 in. in diameter, and standard length for full size specimen. It was felt that samples prepared in this way would have experienced the least possible amount of surface damage. Each value tabulated is the average value of eight determinations. This method of determining impact resistance was found to be extremely consistent. However, the absolute values tabulated are not well established because the capacity of the particular impact machine at hand was so large that all readings represent extrapolated values from a difference of less than one degree in arc swing. A more sensitive impact machine has been located at MERL, Pratt & Whitney Aircraft, Middletown and will be used to verify these values as soon as new samples can be prepared.

As Table III shows, UARL 304 has the highest impact resistance and UARL 459 has the lowest impact resistance of the glasses evaluated. The composition of UARL 304 contains both aluminum oxide and zinc oxide and this combination apparently contributes to its increased impact resistance since UARL 447 which contains zinc oxide but not alumina is low in impact resistance as is UARL 419 which contains alumina but not zinc oxide. Obviously, these are very preliminary clues as to the factors important in impact resistance and the dependence of impact resistance on composition must be much more carefully investigated.

Table II

Recently Measured Values for Young's Modulus
(Circular Rod Bulk Samples)

Glass No.	Density gms/cm^3	Density lbs/in^3	Young's Modulus millions psi	Specific Modulus 10^7 inches
134	3.0983	0.1116	15.61	14.0
152	4.3834	0.1580	15.27	9.63
160	3.2452	0.1170	15.95	13.65
345B	3.3594	0.1216	19.82	16.32
*425B	2.7561	0.0995	18.19	18.24
467	3.4302	0.1238	15.63	12.65
468	3.4426	0.1242	15.48	12.45
469	3.3773	0.1219	15.25	12.54
470	3.3020	0.1193	16.02	13.43
471	3.1743	0.1145	16.98	14.82
472	3.2183	0.1162	16.93	14.55
473	too high a forming temperature			
474	too high a forming temperature			
475	too high a forming temperature			
**476			17.28	
477			17.91	
478			17.90	
479				
480			17.33	
481			17.48	
482			15.87	

*UARL 425 is National Bureau of Standards Glass #389 (Ref. 5)

**UARL 476 is Bastian, U.S. Patent 2,978,341 - maximum amount of ingredients

Table III

Glass Number or Designation	Impact Resistance (in lbs)	Young's Modulus 10^6 psi	Compositions of Glasses Evaluated as Impact Specimens (Mol %)											
			SiO_2	Al_2O_3	MgO	Y_2O_3	BeO	ZnO	Li_2O	La_2O_3	CaO	B_2O_3	ZrO_2	TiO_2
237	0.75	18.3	45	15	30	10								
304	0.85	19.65	35	15	30	10		10						
323	0.59	18.4	35	15	30		10		10					
331	0.82	20.9	39	12		12	25	12						
336	0.80	21.0	35	15		10	30	10						
344	0.79	20.3	45	15	15	10	15							
347	0.82	21.6	50	8.33		25		8.33		8.33				
350	0.71	19.8	24	11	11		20		11		11			
383	0.71	22.75	24	3	16			8	12		12	10	12	3
417	0.71	19.35	45	15	15	7	15		3					
419	0.64	20.15	42	15	15	10			3					
425	0.54	19.51	42.9	7	25.6		24.6							
447	0.595	18.23	25		15	12		10	10		15	13		
459	0.48	17.34	25		15	10		14	14		14	8		
"E"	0.625	10.5	57	8.9	7.1						19.7	7.1		

The mechanism by which UARL 304 gained appreciably increased impact resistance compared to UARL 459 is shown in Figs. 1 and 2 where optical macrographs showing typical fracture systems in these two glasses are compared. The much larger initiation zone, mist zone, and hackle zone for glass UARL 304 (Fig. 1) shows that it absorbed more energy before fracturing than did UARL 459 (Fig. 2). While these figures are from only one specimen of each glass, other specimens of the subject glasses showed identical behavior and it is felt that more sensitive impact testing equipment will show that the ratio of the comparative impact resistances of these two glasses is much larger than the factor of two currently shown in our Table III.

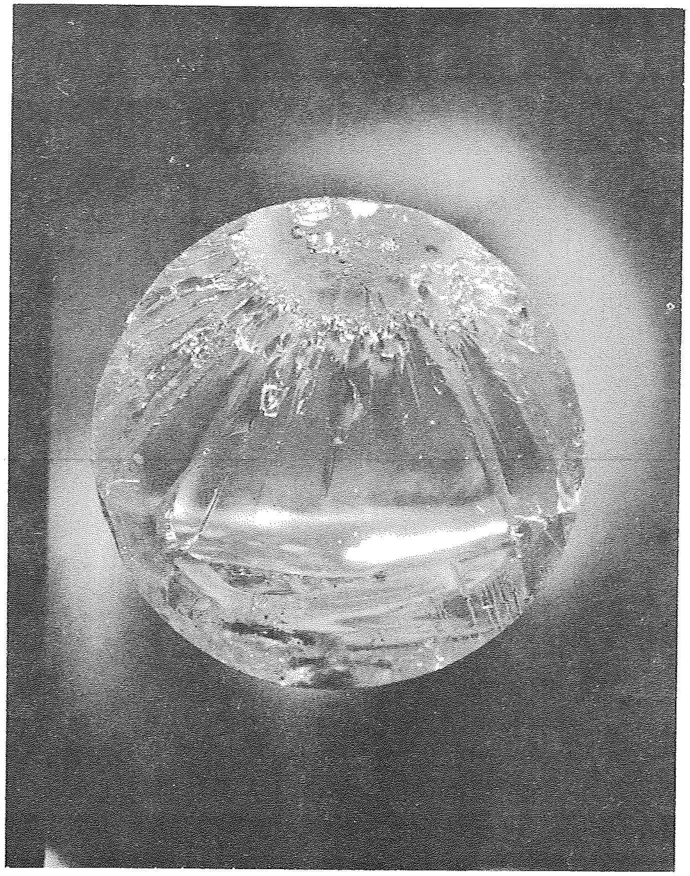
IMPROVED COMPRESSIVE STRENGTH MEASUREMENTS

Last quarter, UARL attempted to evaluate the compressive strength of UARL 417-epoxy resin composites. Unfortunately, the currently accepted test method for this property was developed for available materials with ultimate values so much lower than that accepted for the new composites that they actually are not suitable. Further the basic structure of glass fiber composites can not conform within normal test limits to small variations in positioning the specimen, in the alignment of the loading force, and in the surface effect of load application.

Celanese Corporation (Ref. 6) had already faced this problem in testing the compressive strength of their graphite-epoxy resin composites. To at least partially eliminate the problem they designed a compression jig which allows the compressive force to be induced by shear stresses on bonded tabs in a collet type grip which does not come in contact with the test specimen. Using the Celanese Corporation design jig we were able to completely eliminate the mushrooming effect found in our earlier tests as well as obtaining gage-length failures which appear reasonable. The average compressive strength found for the UARL 417 glass fiber-compression strength composites with the Celanese type jig is 222,000 psi as shown in Table IV. In our opinion this still represents a lower limit for this type of test and further testing should raise this value appreciably. The relationship of the compressive strength of the UARL 417 glass fiber-epoxy resin composites to the similar much lower compressive strength composites with the DuPont organic fiber PRD-49 is also shown in Table IV.

COMPARISON OF SEVERAL FIBER-RESIN COMPOSITES

In Table V the properties of four epoxy resin-fiber composites are compared. The "S" glass, UARL 344, and UARL 417 glass fiber-epoxy resin composites were all made in this laboratory using identical procedures but the data for the DuPont PRD-49-I fiber composite was taken from DuPont brochures. The data of Table V shows that the glass fiber-epoxy resin composites are superior in flexural strength (both absolute and specific), short-beam shear strength (both absolute and specific), compressive strength (both absolute and specific), impact-strength,



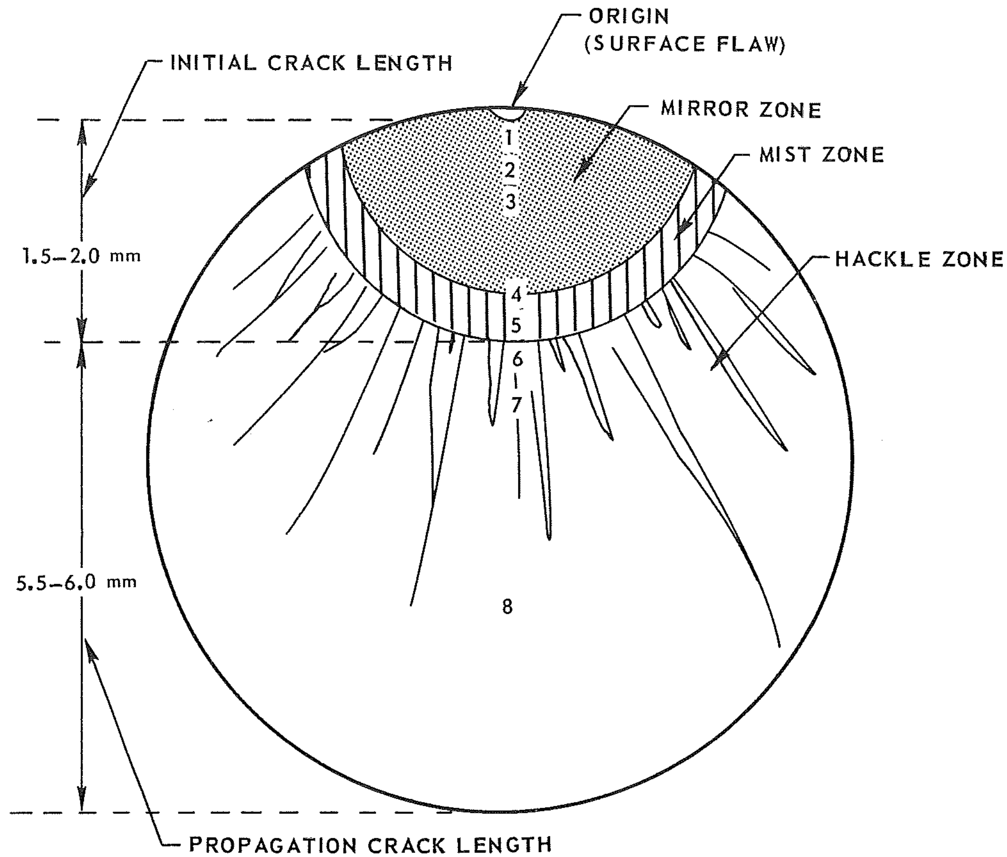
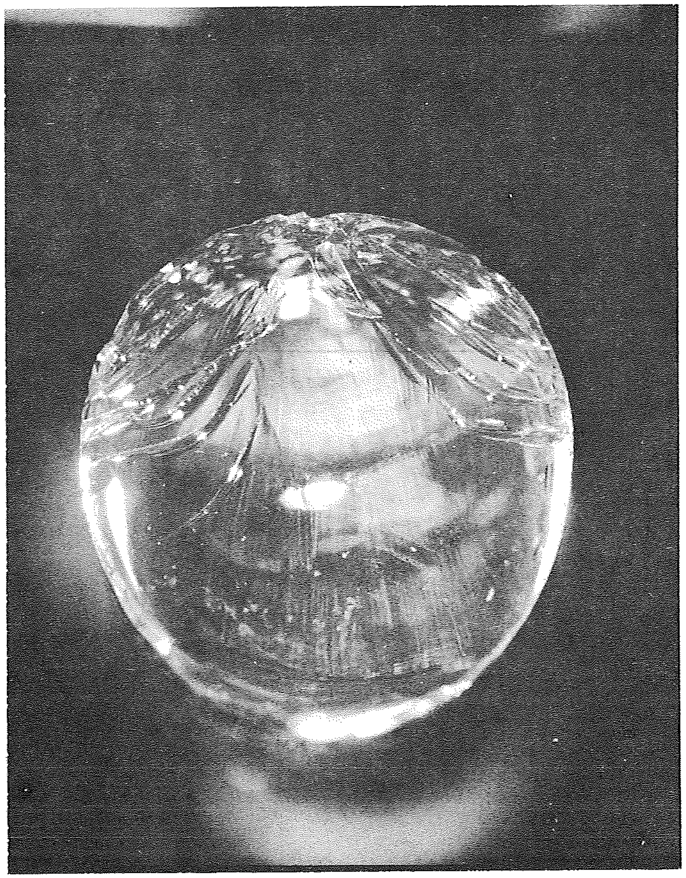


FIG. 1 OPTICAL MACROGRAPH AND SKETCH OF REPRESENTATIVE SAMPLE OF UARL NO. 304



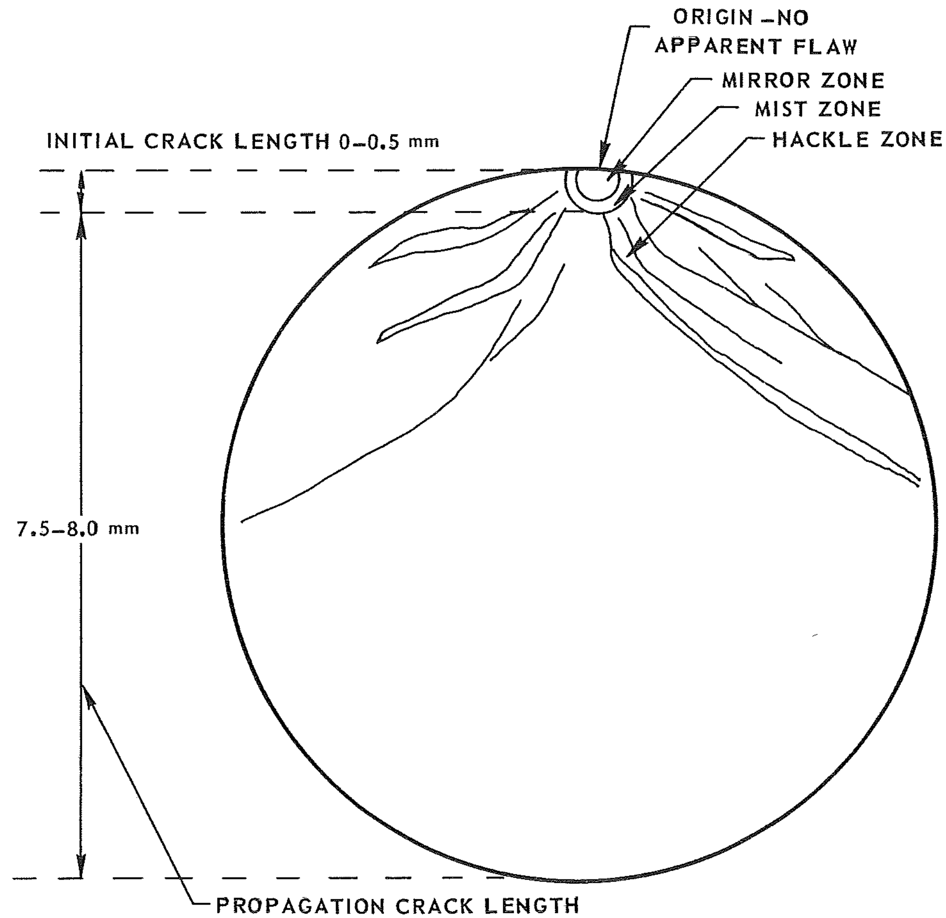


FIG. 2 OPTICAL MACROGRAPH AND SKETCH OF REPRESENTATIVE SAMPLE OF UARL NO. 459

Table IV

Ratio of Compressive Strength to Density

Material	Density lb/in.^{3}	Compressive Strength lbs/in.^{2}	Specific Compressive Strength (in.)
UARL 417/epoxy	0.092	218-227,000	2,370,000-2,470,000
*PRD-49I/epoxy	0.050	35-50,000	700,000-1,000,000
*Graphite/epoxy	0.053	50-110,000	900,000-2,100,000
*Aluminum			
7075-T6	0.101	73,000	730,000
2024-T6	0.100	47,000	470,000
*Titanium			
6Al-4V	0.16	155,000	970,000

*Data from DuPont's Brochure, New High-Modulus Fiber, PRD-49, Type 1, as presented at Anaheim, California meeting, April 1971.

Table V

Comparison of Several Fiber-Resin Composites

Composite and Glass Identity	634 (S glass)	Average of 7 Composites UARL 344	695* UARL 344	UARL 417	DuPont PRD-49-I
Fiber Finish	Commercial	Proprietary	Proprietary	Proprietary	None
% Voids	0.6	3.1	2.5	1.0	--
% Fiber	67	62	60	71.5	65
Density of Composite gms/cm^3	2.07	2.47	2.49	2.55	1.38
Flexural Strength 10^3 psi	215	254	290	228	95
Flexural Modulus 10^6 psi	---	11.3	11.2	12.07	17
Short Beam Shear Strength 10^3 psi	13.9	14.4	16.7	15.5	7.5
Tensile Strength 10^3 psi	266	250	250	298	200
Tensile Modulus 10^6 psi	8.27*	10.9	10.9	11.9	14.0
Notched Charpy Impact Value ft. lbs/in^2	435	242	242	214	150
Compressive Strength 10^3 psi				218-227	40-50

S glass has a density of 2.49 gms/cm^3 and a Young's Modulus of 12.4 x 10^6 psi.
UARL 344 glass fiber has a density of 3.29 gms/cm^3 and a Young's Modulus of 18.6 x 10^6 psi.
UARL 417 glass fiber has a density of 3.09 gms/cm^3 and a Young's Modulus of 17.5 x 10^6 psi.
DuPont PRD-49-I organic fiber has a density of 1.38 gms/cm^3 and a Young's Modulus of 20 x 10^6 psi.

*Estimate based on fiber % and known modulus of glass.
**Results obtained after an initial series of learning experiments had been carried out in making and testing UARL 344 glass fiber-epoxy resin composites.

and in absolute tensile strength in comparison to the DuPont PRD-49-I epoxy resin composite. This absolute strength of the UARL fiber-epoxy resin composite indicates a very high strength retention for the UARL 417 fiber without sizing and after the considerable amount of handling necessary to form a glass fiber-epoxy resin matrix.

In our last quarterly report, K911105-1, tensile stress-strain curves and bending stress-strain curves for UARL 417 glass fiber-epoxy resin composites and DuPont PRD-49-I fiber-epoxy resin composites were also compared and, in both cases, the comparison was favorable to the UARL 417 glass fiber composite.

CONCLUSIONS

1. Bulk samples of selected experimental UARL glasses vary in impact strength by approximately a factor of two in the latest impact test procedure. Preliminary indications are that composition affects the impact strength and that both aluminum oxide and zinc oxide are necessary for increased impact strength. However, much more work remains to be done on the test procedure and other glasses need to be examined before any definite conclusions can be reached in this area.

2. Additional tests on UARL 417 fiber glass-epoxy resin composites show these composites to be better than DuPont PRD-49 fiber-epoxy resin composites in all properties concerned with compression, bending and flexure and comparable in tensile properties.

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